INTERMITTENT FEEDING TECHNIQUE FOR INCREASING THE MELTING RATE OF POLYCRYSTALLINE SILICON

BACKGROUND

The present invention generally relates to the production of single crystal silicon, and specifically, to a process for feeding granular polycrystalline silicon while preparing a silicon melt.

Most single crystal silicon used for microelectronic circuit fabrication is prepared by the Czochralski (CZ) process. In this process, a single crystal silicon ingot is produced by melting polycrystalline silicon in a crucible, dipping a seed crystal into the silicon melt, withdrawing the seed crystal in a manner sufficient to achieve the diameter desired for the ingot and growing the single crystal at that diameter. The polycrystalline silicon melted to form the silicon melt is typically irregularly shaped chunk polycrystalline silicon prepared by the Siemens process or, alternatively, free-flowing, generally spherically-shaped granular polycrystalline silicon, typically prepared by a fluidized-bed reaction process. The preparation and characteristics of chunk and granular polycrystalline silicon are detailed in F. Shimura, Semiconductor Silicon Crystal Technology, pages 116-121, Academic Press (San Diego CA, 1989) and the references cited therein.

The initial charging of chunk type polycrystalline silicon into the crucible and the melting thereof can introduce undesirable impurities and defects into the single crystal silicon ingot. For example, when a crucible is initially charged entirely with chunk polycrystalline silicon, the edges of the chunks under the load of a full charge can scratch and gouge the crucible wall, resulting in a damaged crucible and in particles of crucible floating on or being suspended in the silicon melt. These impurities significantly increase the likelihood of dislocations forming within the single crystal, and decrease the dislocation-free single crystal production yields and throughput. Careful arrangement of the chunk polycrystalline silicon during the initial loading can minimize the thermal stresses. As melting proceeds, however, the charge can shift or the lower portion of the chunk polycrystalline silicon can melt

away and leave either a "hanger" of unmelted material stuck to the crucible wall above the melt or a "bridge" of unmelted material bridging between opposing sides of the crucible wall over the melt. When the charge shifts or a hanger or bridge collapses, it may splatter molten silicon and/or cause mechanical stress damage to the crucible. Additionally, initial loadings of 100% chunk polycrystalline silicon limit the volume of material which can be charged due to the poor packing densities of such chunk materials. The volume limitations directly impact single crystal throughput.

Problems also exist when a CZ crucible is initially charged entirely with granular polycrystalline silicon. Large amounts of power are required to melt the granular polycrystalline due to its low thermal conductivity. The thermal stress induced in the crucible by exposure to such high meltdown-power can cause distortion of the crucible and particles of the crucible to be loosened and suspended in the melt. Like the mechanical stresses, these thermal stresses result in reduced zero-defect crystal production yields and throughput. Thus, to avoid the thermal stresses, loadings of 100% granular polycrystalline silicon are typically of a smaller size which reduces overall throughput.

Whether the crucible is initially loaded with chunk or granular polycrystalline silicon, in many processes it is desired to add polycrystalline silicon to the melt with a feeding/metering system to increase the quantity of molten silicon. The use of such additional loadings of charge-up polycrystalline silicon is known for batch, semi-continuous or continuous process systems. In the batch system, for example, additional silicon may be loaded into the existing melt to achieve full crucible capacity in light of the decrease in volume after the initial polycrystalline silicon charge is melted. Japanese Utility Model Application No. 50-11788 (1975) is exemplary. In semi-continuous and continuous CZ systems, additional polycrystalline silicon is charged to the silicon melt to replenish the silicon withdrawn as the single crystal. F. Shimura, <u>Semiconductor Silicon Crystal Technology</u>, p. 175-83, Academic Press (San Diego CA, 1989).

Although granular polycrystalline silicon is generally the material of choice to replenish batch, semi-continuous and continuous CZ systems because of its free-flowing form, it is not without its disadvantages. As disclosed by Kajimoto et al. in U.S. Patent No. 5,037,503, granular polycrystalline silicon prepared by the silane process contains hydrogen in an amount sufficient to cause the silicon granules to burst or explode when they are immersed in molten silicon. The explosion or bursting of the polycrystalline silicon granules causes scattered silicon droplets to accumulate on the surface of the crucible and other components in the crystal puller which can fall into the molten silicon and interrupt crystal growth. As a solution to this problem, Kajimoto et al. suggest reducing the hydrogen content of the granular polycrystalline silicon by preheating the granular polycrystalline in an inert gas atmosphere in a separate heating apparatus until the concentration of H_2 is 7.5 ppm by wt. (210 ppma) or less. While this approach tends to reduce the force with which the granules explode, it does not eliminate the phenomena. Rather, the bursting phenomena can still be experienced with granular polycrystalline having a hydrogen concentration of less than 1 ppm by wt. (28 ppma). To date, granular polycrystalline silicon is available in commercial quantities having a hydrogen concentration ranging from about 0.4 to about 0.7 ppm by wt. (11-20 ppma).

An alternative solution to this problem is disclosed by Holder in U.S. Patent No. 5,588,993, wherein chunk polycrystalline silicon is partially melted and then granular polycrystalline silicon is continuously fed onto the exposed unmelted portion of the chunk polycrystalline silicon (column 4, line 66 to column 5, line 4). The granular polycrystalline silicon is fed at a rate which allows for it to reach a temperature greater than about 1200 °C and remain at this temperature for about 30 seconds before melting. Heating the granular polycrystalline silicon in this manner allows for it to be dehydrogenated before becoming immersed in the silicon melt. A less than desirable characteristic with such an approach is that the continuous feeding of granular polycrystalline silicon is limited to a relatively slow rate (e.g., about 8-12 kg/hr) which extends the feeding time and thereby increases the time

required to prepare the silicon melt. For example, the time typically required to prepare a 80 kg silicon melt is about 7-8 hours, thus acting to reduce the crystal puller throughput, especially as the average hydrogen content of the granular polycrystalline silicon feed exceeds about 10 ppma. For a 100 and a 120 kg silicon melt, the typical melt down time is about 10 and 12 hours, respectively. This relatively slow feed rate is due, in large part, to the crucible limitations discussed above. Specifically, the power necessary to increase the melt down rate of the granular polycrystalline silicon would distort the crucible and result in crucible particles being suspended in the melt.

As a result, a need continues to exist for a process whereby polycrystalline silicon can be melted more quickly to form silicon melts while maintaining the yield of dislocation-free single crystal silicon ingots produced from these melts.

SUMMARY OF THE INVENTION

Among the objects of the present invention, therefore, is the provision of a process whereby polycrystalline silicon can be melted more quickly to form silicon melts; the provision of a polycrystalline feed and melt process which maintains a yield of dislocation-free single crystal silicon ingots produced from these melts; the provision of feed process which allows for fed granular polycrystalline silicon to be dehydrogenated before becoming immersed in the silicon melt; and the provision of a process whereby the location onto which polycrystalline silicon is fed is controlled.

Briefly, therefore, the present invention is directed to process for preparing a silicon melt in a crucible for use in growing a single crystal silicon ingot by the Czochralski method. The process comprises forming a partially melted charge in the crucible, the partially melted charge comprising molten silicon and unmelted polycrystalline silicon, the molten silicon having an upper surface, the unmelted polycrystalline silicon comprising an exposed portion that is above the upper surface of the molten silicon. The process further comprises rotating the crucible and feeding polycrystalline silicon into the rotating crucible by intermittently delivering the

fed polycrystalline silicon onto the exposed unmelted polycrystalline silicon. The intermittent delivery comprises a plurality of alternating on-periods and off-periods, wherein each on-period comprises flowing the fed polycrystalline silicon through a feed device that directs the flow of the fed polycrystalline silicon onto the unmelted polycrystalline silicon for an on-duration, and each off-period comprises interrupting the flow of the fed polycrystalline silicon for an off-duration. The process further comprises melting the unmelted polycrystalline silicon and the fed polycrystalline silicon to form the silicon melt.

The present invention is also directed to a process for preparing a silicon melt in a crucible. The process comprises loading the crucible with polycrystalline silicon and rotating the loaded crucible. Heat is applied to the loaded polycrystalline silicon to form molten silicon and unmelted polycrystalline silicon, the molten silicon comprising an upper surface, the unmelted polycrystalline silicon comprising an exposed portion that is above the upper surface of the molten silicon. Polycrystalline silicon is then fed into the rotating crucible by intermittently delivering the fed polycrystalline silicon onto the exposed unmelted polycrystalline silicon, the intermittent delivery comprising a plurality of alternating on-periods and off-periods, wherein each on-period comprises flowing the fed polycrystalline silicon through a feed device that directs the flow of the fed polycrystalline silicon onto the unmelted polycrystalline silicon for an on-duration, and each off-period comprises interrupting the flow of the fed polycrystalline silicon for an off-duration. The loaded polycrystalline silicon and the fed polycrystalline silicon are melted to form the silicon melt.

The present invention is also directed to a process for preparing a silicon melt in a crucible for use in growing a single crystal silicon ingot by the Czochralski method. The process comprises loading the crucible with polycrystalline silicon, the crucible comprising an interior wall and having an inner diameter (*D*) and rotating the loaded crucible at a rate (r). Heat is applied to the loaded polycrystalline silicon to form molten silicon and unmelted polycrystalline silicon, the molten silicon

comprising an upper surface, the unmelted polycrystalline silicon comprising an exposed portion that is above the upper surface of the molten silicon. The exposed unmelted polycrystalline has a center and a width (*d*) that corresponds to the longest distance between two points along the interface between the exposed unmelted polycrystalline silicon and the upper surface of the molten silicon. The process further comprises feeding a polycrystalline silicon mass into the rotating crucible by intermittently delivering a portion of the polycrystalline silicon mass at a feed rate (*F*) onto the exposed unmelted polycrystalline thereby maintaining the width (*d*) of the exposed unmelted polycrystalline. The intermittent delivery comprises a plurality of alternating on-periods and off-periods, wherein each on-period comprises flowing polycrystalline silicon at a flow rate (*f*) for a duration (t_{on}) through a feed device that directs the polycrystalline silicon onto the exposed unmelted polycrystalline, and wherein each off-period comprises interrupting the flow of polycrystalline silicon through the feed device for a duration (t_{off}). Also, melting the loaded polycrystalline silicon and the fed polycrystalline silicon are melted to form the silicon melt.

The present invention is also directed to a process for preparing a silicon melt by loading a crucible with chunk polycrystalline silicon, the amount of the chunk polycrystalline silicon load being between about 40% to about 65% of the total amount of the polycrystalline silicon melted to form the silicon melt. The process further comprises rotating the loaded crucible and heating the loaded chunk polycrystalline silicon to form molten silicon and unmelted polycrystalline silicon. The molten silicon comprises an upper surface. The unmelted polycrystalline silicon comprises an exposed portion that is above the upper surface of the molten silicon, the exposed unmelted polycrystalline having a center and a width that corresponds to the longest distance between two points along the interface between the exposed unmelted polycrystalline silicon and the upper surface of the molten silicon. The interface between the unmelted polycrystalline silicon and the upper surface of the molten silicon is also approximately equidistant from the center of the unmelted polycrystalline silicon. The process further comprises feeding a granular

polycrystalline mass into the rotating crucible by intermittently delivering a portion of the granular polycrystalline silicon mass onto the exposed unmelted polycrystalline silicon thereby maintaining the width of the exposed unmelted polycrystalline silicon, the intermittent delivery comprising a plurality of alternating on-periods and off-periods. Each on-period comprises flowing the granular polycrystalline silicon through a feed device that directs the granular polycrystalline silicon onto a wedge of the exposed unmelted polycrystalline silicon that does not substantially overlap with the immediately preceding wedge. Each off-period comprises interrupting the flow of polycrystalline silicon through the feed device. Also, the process comprises melting the loaded polycrystalline silicon and the fed polycrystalline silicon to form the silicon melt.

The present invention is also directed to a process for preparing a silicon melt comprising loading a crucible, comprising an interior wall and an inner diameter, *D*, with chunk polycrystalline silicon, the amount of the chunk polycrystalline silicon load being between about 40% to about 65% of the total amount of the polycrystalline silicon melted to form the silicon melt. The process further comprises rotating the loaded crucible at a rate that ranges from about 1 rpm to about 5 rpm and heating the loaded chunk polycrystalline silicon to form molten silicon and unmelted polycrystalline silicon. The molten silicon comprising an upper surface and the unmelted polycrystalline silicon comprising an exposed portion that is above the upper surface of the molten silicon that has a center and a width, *d*, that corresponds to the longest distance between two points along the interface between the exposed unmelted polycrystalline silicon and the upper surface of the molten silicon. The interface between the unmelted polycrystalline silicon and the upper surface of the molten silicon is approximately equidistant from the center of the unmelted polycrystalline silicon and is approximately equidistance from the interior wall of the crucible. The process further comprises feeding a granular polycrystalline mass into the rotating crucible by intermittently delivering a portion of the granular polycrystalline silicon mass onto the exposed unmelted polycrystalline silicon

thereby maintaining the width of the exposed unmelted polycrystalline silicon, d, at about 65% to about 85% of the crucible diameter, D. The intermittent delivery comprises a plurality of alternating on-periods and off-periods, wherein each on-period comprises flowing the granular polycrystalline silicon at a flow rate, f, of about 5 g/s to about 35 g/s for duration, t_{on}, of about 2 seconds to about 10 seconds through a feed device that directs the granular polycrystalline silicon onto a wedge of the exposed unmelted polycrystalline silicon wherein each wedge has a wedge angle of about 40° to about 72° and each wedge does not substantially overlap with the immediately preceding wedge. Each off-period comprises interrupting the flow of polycrystalline silicon through the feed device for a duration, t_{off}, of at least about 5 seconds. The process further comprising melting the loaded polycrystalline silicon and the fed polycrystalline silicon to form the silicon melt.

The present invention is also directed to a process for preparing a silicon melt in a crucible. The process comprises rotating the crucible at a rate (r) and forming a depleted molten silicon charge in the rotating crucible, the depleted molten silicon charge having a weight, w, the crucible comprising an interior wall and having an inner diameter (D). The process further comprises feeding polycrystalline silicon into the rotating crucible by delivering the polycrystalline silicon onto the depleted molten silicon charge to form a partial charge comprising molten silicon and unmelted polycrystalline silicon. The molten silicon comprises an upper surface. The unmelted polycrystalline silicon comprises an exposed portion that is above the surface of the molten silicon, the exposed unmelted polycrystalline silicon having a center and width (d) that corresponds to the longest distance between two points along the interface between the exposed unmelted polycrystalline silicon and upper surface of the molten silicon. The process further comprises feeding polycrystalline into the rotating crucible by intermittently delivering polycrystalline silicon onto the exposed unmelted polycrystalline silicon thereby maintaining the width of the exposed unmelted polycrystalline silicon (d), the intermittent delivery comprising a plurality of alternating on-periods and off-periods, wherein each on-period comprises

flowing polycrystalline silicon at a flow rate (f) for a duration (t_{on}) through a feed device that directs the polycrystalline silicon onto the exposed unmelted polycrystalline silicon, and wherein each off-period comprises interrupting the flow of polycrystalline silicon through the feed device for a duration (t_{off}). The process further comprises melting the unmelted polycrystalline silicon and the intermittently delivered polycrystalline silicon to form the silicon melt.

Other objects and features of this invention will be in part apparent and in part pointed out hereinafter

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a section view of a Czochralski crucible showing an initial loading of chunk polycrystalline silicon.

FIG. 2 is a section view showing the commencement of the intermittent feed process of the present invention wherein granular polycrystalline silicon is fed into the crucible using an off-center vertical feed tube.

FIG. 3 is a section view showing a subsequent on-period of the intermittent feed process of the present invention wherein granular polycrystalline silicon is fed into the crucible using an off-center vertical feed tube.

FIG. 4 is a section view showing the completion of the feeding of granular polycrystalline silicon.

FIG. 5 is a section view showing a silicon melt.

FIG. 6 is a section view showing the commencement of the intermittent feed process of the present invention wherein granular polycrystalline silicon is fed into the crucible using a spray feed tube.

FIG. 7 is a section view showing a subsequent on-period of the intermittent feed process of the present invention wherein granular polycrystalline silicon is fed into the crucible using a spray feed tube.

FIG. 8 contains three views of feeding patterns which may be produced using the intermittent feeding processes of the present invention.

FIG. 9 contains three views of feeding patterns which may be produced using the intermittent feeding processes of the present invention.

FIG. 10 contains a view of a feeding pattern which may be produced using the intermittent feeding processes of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, a partially melted charge is formed in a Czochralski (CZ) crucible, the partially melted charge comprising molten silicon and unmelted polycrystalline silicon, the molten silicon having an upper surface, the unmelted polycrystalline silicon comprising an exposed portion that is above the upper surface of the molten silicon. Typically, the partially melted charge is formed by one of or a combination of the following methods: (a) initially loading the crucible with polycrystalline silicon and heating the loaded polycrystalline silicon to form the molten silicon and the unmelted polycrystalline silicon; and/or (b) feeding polycrystalline onto a depleted molten silicon charge to form a partial charge comprising the molten silicon and the unmelted polycrystalline silicon. In accordance with the present invention, additional polycrystalline silicon is fed into the crucible by intermittently delivering polycrystalline silicon onto the exposed unmelted polycrystalline silicon in a manner which preferably decreases the amount of time required to prepare a fully molten silicon melt compared to a continuous feeding method. The invention is described in further detail below with reference to the figures, in which like items are numbered the same in the several figures.

With reference now to FIG. 1, polycrystalline silicon **10** is loaded into a standard Czochralski crucible **20**. Although either granular polycrystalline silicon or chunk polycrystalline silicon could be used for the initial loading, chunk polycrystalline silicon is preferred. The use of granular polycrystalline silicon for the initial loading can result in relatively poor production yields and a high incidence of large void defects forming in the single crystal silicon ingot. It is believed that the granular polycrystalline silicon traps gasses such as argon or hydrogen at the

bottom **24** of the crucible **20**, and that these gasses later release as bubbles into the silicon melt during crystal growth. Some of the bubbles become attached to the crystal at the crystal growth interface, thus forming void defects. The use of chunk polycrystalline silicon for the initial loading avoids the formation of these void defects, and generally results in higher yields.

The amount of polycrystalline silicon initially loaded into the crucible is preferably optimized with respect to the quality of the single crystal silicon ingot and production throughput. If too much chunk polycrystalline silicon is loaded into the crucible, higher mechanical stresses occur, and there is also an increased probability of the charge shifting or forming bridges or hangers. Economic, availability or other factors favoring granular polycrystalline silicon may also encourage minimizing the amount of chunk polycrystalline silicon in the initial load. If too little chunk polycrystalline silicon is loaded, however, a considerably greater amount of power is required to melt the charge. The higher wall temperatures associated with the use of such higher power can result in premature crucible degradation. In addition to these factors, the initial loading size will also vary with crucible design, hot zone design and the types of crystal products being produced. Preferably, the weight of the initial loading of chunk polycrystalline silicon is about 40% to about 65% of the total melt weight and more preferably about 50% to about 60% of total melt weight.

Preferably, the initial load of chunk polycrystalline silicon is arranged in the crucible with the center **12** of the polycrystalline silicon **10** being higher than the edge **14**. For example, when preparing the initial 40 kg load of an 80 kg total charge, the center is preferably about 23.5 to about 31 mm higher than the edge. This preferred arrangement along with the preferred amount of initially loaded chunk ensure that the height of the chunk polycrystalline silicon at the edge **14** is less than the height of the completed silicon melt thereby preventing the formation of hangers and/or bridges above the silicon melt. During the melt down, the position of the crucible **20** is such that its top edge **22** is about 10-80 mm above the top edge **32** of

the side heater **30**, and preferably about 50 mm. This crucible position is preferably maintained constant for the duration of the meltdown.

As shown in FIG. 2, the loaded polycrystalline silicon **10** is heated (while rotating the crucible at a rate (*r*)) to form molten silicon **16** and unmelted polycrystalline silicon **11**. The molten silicon **16** has an upper surface **18** above which a portion of the unmelted polycrystalline silicon **11** is exposed. The exposed unmelted polycrystalline having a center **12** and a width **52** that corresponds to the longest distance between two points along the interface between the exposed unmelted polycrystalline silicon and the upper surface of the molten silicon **53**. Preferably, the interface **53** is substantially circular, or stated another way, the interface **53** is approximately equidistant from the center **12** of the exposed unmelted polycrystalline silicon (e.g., a variation of less than about 20% and preferably less than about 10%. The exposed unmelted polycrystalline silicon **11** is essentially an island surrounded by the molten silicon **16** that is formed by heating the crucible **20** with a side heater **30**. To partially melt an initial loading of 40 kg of chunk polycrystalline silicon in a 20 inch (about 51 cm) diameter crucible, for example, the side heater **30** is maintained at a power level of 118 kW. Although the position of the exposed unmelted polycrystalline silicon can vary in the crucible (i.e., the island may move because of floating), the central axis **50** of the crucible preferably passes through the exposed unmelted polycrystalline silicon near the center **12** (e.g., within about 5 cm). Thus, the interface **53** preferably remains approximately equidistant from interior wall **21** of the crucible (e.g., a variation of less than about 20% and preferably less than about 10%.

The extent to which the initial load of polycrystalline silicon is melted to form the polycrystalline silicon island may be specifically defined with respect to the relative amounts of molten silicon **16** and unmelted polycrystalline silicon **11**. By this measure, the ratio of molten silicon **16** to unmelted polycrystalline silicon **11** in the partially melted charge is between about 3:2 and about 4:1 by weight. Alternatively, the extent of melting may be defined with respect to the diameter of the crucible.

Preferably, the width **52** of the exposed unmelted polycrystalline silicon (*d*) is between about 65% to about 85% of the crucible diameter (*D*) and still more preferably at about 75% of the crucible diameter. A 40 kg charge was partially melted using the heater power value recited above in about four hours.

In accordance with the present invention, after partially melting the initial load in the crucible, additional polycrystalline silicon is fed into the crucible by intermittently delivering polycrystalline silicon onto the exposed unmelted polycrystalline thereby maintaining the width of the exposed unmelted polycrystalline (*d*) within the above recited values. The intermittent delivery comprising a plurality of alternating on-periods and off-periods wherein each on-period comprises flowing polycrystalline silicon at a flow rate (*f*) for a duration (t_{on}) through a feed device that directs the polycrystalline silicon onto the exposed unmelted polycrystalline silicon, and each off-period comprises interrupting the flow of polycrystalline silicon for a duration (t_{off}). The flow rate (*f*), the on-period duration (t_{on}) and the off-period duration (t_{off}) of the intermittent delivery result in feeding the polycrystalline silicon into the crucible at a feed rate (*F*).

As stated above, the foregoing feed parameters are preferably controlled so that polycrystalline silicon is fed onto the exposed unmelted polycrystalline thereby maintaining the diameter of the island between about 65 and about 85% of the diameter of the crucible and more preferably at about 75% of the diameter of the crucible for the most efficient melting without causing crucible damage by over heating the crucible. Specifically, if the island becomes too large (e.g., greater than about 85% of the crucible diameter) the island may touch the wall of the crucible and "freeze over" due to the heat sink effect (i.e., the emissivity of the solid is so much higher than liquid silicon). On the other hand, if the island is too small (e.g., less than about 65% of the crucible diameter), the crucible is damaged by the hotter than necessary temperature.

Experimental results to date suggest that the rotation rate of the crucible (*r*) is at least about 1 rpm, the flow rate of granular polycrystalline(*f*) is at least about 1 g/s,

the duration of each on-period (t_{on}) is at least about 1 second, the duration of each off-period(t_{off}) is at least about 1 second, and the feed rate of the intermittently delivered granular polycrystalline silicon(F) is at least about 1 kg/hr. Preferably, the rotation rate (r) ranges from about 1 rpm to about 5 rpm and more preferably from about 2 rpm to about 3 rpm. Preferably, the flow rate of granular polycrystalline (f) ranges from about 5 g/s to about 35 g/s and more preferably from about 10 g/s to about 25 g/s. Preferably, the duration of each on-period (t_{on}) ranges from about 2 seconds to about 10 seconds and more preferably from about 4 seconds to about 10 seconds. Preferably, the duration of each off-period (t_{off}) is at least about 5 seconds, more preferably it ranges from about 10 seconds to about 30 seconds, still more preferably from about 10 seconds to about 20 seconds and even more preferably from about 10 seconds to about 15 seconds. Preferably, the feed rate of the intermittently delivered granular polycrystalline silicon (F) ranges from about 1.5 kg/hr to about 65 kg/hr, more preferably from about 5 kg/hr to about 30 kg/hr, and still more preferably from about 10 kg/hr to about 20 kg/hr.

The polycrystalline silicon fed onto the exposed unmelted polycrystalline silicon is preferably granular polycrystalline silicon. Preferably, the granular polycrystalline silicon is dust free and 90% of the granules (by weight) have a size distribution falling within the range of about 400μm to about 1400μm. The type and hydrogen concentration of the granular polycrystalline silicon used in the preferred embodiment of the present invention is not critical as long as the feed rate and other process parameters are controlled to ensure adequate dehydrogenation. The present invention allows the use of granular polycrystalline silicon having a wide range of hydrogen concentrations, including concentrations up to about 500 ppma. Preferably, the hydrogen concentration of the granular polycrystalline silicon fed onto the unmelted polycrystalline silicon is less than about 400 ppma, more preferably less than 50 ppma, and most preferably less than about 20 ppma.

When forming a silicon melt in an accordance with the method of the present invention, it is preferred that the flow, or metering, of the granular polycrystalline

silicon is controlled using a delivery device that comprises what is commonly referred to as an angle of repose valve. Preferably, the present invention is carried out using the device described in greater detail by Boone et al. in U.S. Pat. No. 5,059,410 which is commercially available from Crystal Growth Systems of Hanau, Germany. Among the benefits of using a device which comprise an angle of repose valve are increased purity of the grown silicon ingot and longer equipment life due to the decrease in wear from the abrasive granular polycrystalline silicon.

It has been discovered that the melt down can be further influenced by controlling the manner in which the granular polycrystalline silicon is fed onto the exposed unmelted polycrystalline silicon. Specifically, in accordance with the method of the present invention, the polycrystalline silicon is preferably fed in a manner that directs the flow of polycrystalline on a discreet portion of the exposed unmelted polycrystalline silicon. In contrast, continuous feeding method such as described by Holder in U.S. Patent No. 5,588,993 deposits polycrystalline silicon on the center of the exposed unmelted polycrystalline silicon which results in the formation of a conical shaped mass of unmelted polycrystalline silicon having a slope corresponding to the angle of repose. As the granular polycrystalline silicon is fed upon the center (top) of the cone, it travels down the sloping side of the cone along random pathways.

In one embodiment of the present invention, the polycrystalline silicon is fed onto the exposed unmelted polycrystalline silicon as shown in FIGS. 2 and 3. Specifically, the granular polycrystalline silicon **40** is fed onto the exposed unmelted polycrystalline silicon **11** through a vertical-type quartz glass feed tube **42** (such as those commercially available from Quartz Scientific of Cleveland, Ohio). Prior to and during feeding of the granular polycrystalline silicon, the feed tube **42** is movably positioned slightly off the center line **50** of the crucible **20** (e.g., about 10 mm to about 20 mm) and/or slightly away from directly above the center **12** of the exposed unmelted polycrystalline silicon **11**. Feeding commences when the partially melted charge is formed, as defined earlier. By positioning the vertical-type feed tube **42**

off-center, the granular polycrystalline silicon **40** is not randomly deposited over the entire exposed unmelted polycrystalline silicon, rather, it is deposited on a portion of the exposed unmelted polycrystalline silicon. Preferably, that portion is a wedge **63** that extends radially outward from about the center **12** of the unmelted polycrystalline silicon to the interface **61** between unmelted polycrystalline silicon and the upper surface of the molten silicon.

By controlling the melt down parameters (e.g., heater power, rotation rate, on-period duration, off-period duration, flow rate, etc.) in conjunction with the off-center feed tube **42**, the granular polycrystalline silicon preferably forms an island **44** over the surface **13** of the exposed unmelted polycrystalline silicon **11**, with the slope of the island **44** equal to the angle of repose for the granular polycrystalline silicon **40**. For the granular polycrystalline silicon available from MEMC Electronic Materials Inc., the angle of repose is approximately 31 degrees. While the granules of granular polycrystalline silicon **40** are resident on the island **44**, the temperature of the granules rises quickly to result in rapid dehydrogenation before the granules become immersed in the molten silicon **16**. Dehydrogenation of the granular polycrystalline silicon may be effected under the same type of atmospheric conditions, typically under an inert gas, as are known in the art for preparing silicon melts in CZ crucibles. After dehydrogenation, the hydrogen concentration of the granules is less than the saturation concentration of hydrogen in silicon at the melting point of silicon. That is, the concentration of hydrogen after dehydrogenation is less than 1 ppma (0.036 ppm by wt.).

In another embodiment of the present invention, the polycrystalline silicon is fed onto the exposed unmelted polycrystalline silicon as shown in FIGS. 6 and 7. Specifically, the granular polycrystalline silicon **40** is fed onto the exposed unmelted polycrystalline silicon **11** through a spray-type quartz glass feed tube **60** (commercially available from Crystal Growth Systems of Hanau, Germany) which produces a spray of polycrystalline silicon traveling in a direction having a horizontal component. The spray-type feed tube **60** is preferably positioned above the crucible

20 so that the polycrystalline silicon spray deposits on the exposed unmelted polycrystalline silicon **11** in a wedge **64** that is typically larger than the wedge produced using a vertical-type feed tube.

In accordance with the method of the present invention, the melt down process may be further varied by controlling the size of the wedges of granular polycrystalline silicon and the pattern of wedges deposited onto the exposed unmelted polycrystalline silicon. The size of a wedge of polycrystalline silicon fed onto the exposed unmelted polycrystalline silicon is determined, in large part, by the rotation rate and the duration of the on-period (t_{on}). For example, feeding the granular polycrystalline silicon for a duration (t_{on}) of about 7.5 seconds while rotating the crucible at rate (r) of about 2 rpm produces a wedge having a wedge angle of about 90°. Preferably, the wedge has a wedge angle that is less than about 180°. Depending on the process conditions of a particular crystal pulling operation, the size of the wedge can be varied almost infinitely. Experience to date suggests, however, that the wedge angle is preferably less than about 180°, more preferably less than about 120° and still more preferably less than about 90°, and even more preferably ranges from about 40° to about 72°.

As discussed above, the interface between the exposed unmelted polycrystalline silicon and the melted silicon is preferably substantially circular, and in one embodiment of the present invention, the wedge angle is selected such that the substantially circular exposed unmelted polycrystalline silicon can be divided in approximately equal sized segments such as set forth in Table A.

Table A

Wedge Angle	Number of Equal Sized Segments
180°	2
120°	3
90°	4
72°	5
60°	6
51.4°	7
45°	8
40°	9
36°	10
32.7°	11
30°	12
27.7°	13

Preferably, the melt formation parameters such as the crucible rotation rate (r), the on-period duration (t_{on}) and the off-period duration (t_{off}) are controlled so that the flow of granular polycrystalline silicon through the feed device is directed onto a portion of the exposed unmelted polycrystalline silicon (e.g., a wedge) that does not substantially overlap with a portion of the exposed unmelted polycrystalline silicon upon which an immediately preceding on-period polycrystalline silicon feed was deposited (e.g., the immediately preceding wedge). The term substantial overlap is defined herein as being greater than about 30%. More preferably, the overlap is less than about 30%, still more preferably less than about 20%, even more preferably less than about 10%, yet still more preferably less than about 5%, and most preferably there is no overlap.

Depending on the location where and/or the time when the wedges of granular polycrystalline silicon are deposited, the melting rate of the fed granular polycrystalline silicon varies significantly. Experimental results to date suggest that the intermittent feeding process can significantly shorten the feed time compared to a continuous feed process by depositing polycrystalline silicon on the entire exposed unmelted polycrystalline silicon prior to redepositing granular polycrystalline on any wedge. This can be accomplished using a wide variety of feed patterns, some of which are as follows:

(a) each subsequent wedge is deposited adjacent to the immediately preceding wedge and within one rotation of the crucible after the immediately preceding wedge (see, e.g., the 6 segment feed pattern depicted in FIG. 8a wherein the order in which the wedges are deposited is indicated by the numbers within the wedges);

(b) each subsequent wedge is deposited adjacent to the immediately preceding wedge and following at least one rotation of the crucible after the immediately preceding wedge;

(c) each subsequent wedge is deposited nearly opposite from the immediately preceding wedge, and adjacent to the second-most recent wedge and within one rotation of the crucible after the second-most recent wedge (see, e.g., the 3, 7 and 13 segment feed patterns depicted in FIGS. 9a, 9b and 9c); and

(d) each subsequent wedge is deposited nearly opposite from the immediately preceding wedge, and adjacent to the second-most recent wedge and following at least one rotation of the crucible after the second-most recent wedge.

On the other hand, experimental results to date suggest that more frequent deposition of granular polycrystalline silicon on particular portions of the exposed unmelted polycrystalline silicon can significantly lengthen the feed time compared to continuous feed process. Or stated another way, polycrystalline silicon is redeposited on a wedge prior to the depositing granular polycrystalline silicon on the entire exposed unmelted polycrystalline silicon. Referring to FIG. 8b, for example,

the 36° wedges are deposited after about every 108° of crucible rotation which results in redepositing granular polycrystalline silicon on the same location every third on-period. Similarly, the feed pattern depicted in FIG. 8c results in redepositing granular silicon on the same location every other on-period. Feed patterns which lengthen the feed time may be beneficial in circumstances when a heater can only melt the granular polycrystalline silicon at low feed rates (e.g., less than about 15 kg/hr) so that the exposed unmelted polycrystalline silicon does not exceed about 85% of the crucible diameter.

The side heater **30** typically remains energized during the feeding of granular polycrystalline silicon **40** onto the unmelted polycrystalline silicon **11**. For example, when forming an 80 kg melt, the power level of the side heater is maintained at about 118 kW. As shown in FIG. 3, the combined effect of the continued heating during feeding of granular polycrystalline silicon is to result in a solidified silicon mass **46** forming underneath the island **44**. In the preferred embodiment, the solidified silicon mass **46** comprises both chunk polycrystalline silicon from the initial loading and granular polycrystalline silicon from the latter feeding.

Feeding continues in accordance with the parameters of the intermittent delivery process until the total amount of silicon mass desired in the final silicon melt has been charged into the crucible **20**. For an 80 kg total melt mass in which 40 kg of chunk polycrystalline silicon was used for the initial loading, 40 kg of granular polycrystalline silicon **40** must be charged through the feed tube **42**. However, larger total charges may also be realized where the crucible **20** can accommodate the additional silicon melt. After the feeding of granular polycrystalline silicon **40** is complete, the feed tube **42** can be positioned away from the center of the crucible **20** to allow for crystal pulling. At this point, as shown in FIG. 4, the bulk of the silicon in the crucible **20** is molten silicon **16**, with a relatively smaller amount of solidified silicon mass **46** remaining.

The granular polycrystalline silicon and the unmelted polycrystalline silicon, collectively comprising the solidified silicon mass **46**, are further melted to form a

silicon melt. As shown in FIG. 5, the silicon melt comprises 100% molten silicon **16**. When forming an 80 kg melt, the power level for the side heater **30** is preferably maintained at 118 kW to effectuate the final melting in approximately 30 minutes.

To assist in the selection of the intermittent delivery parameters Table B contains the calculated feed rate for various on/off-period combinations and polycrystalline silicon feed rates while rotating the crucible at about 2 rpm.

Table B

Segments	**3**	**4**	**5**	**7**	**6**	**9**	**8**	**13**	**10**	**12**
Time ON (s)	10.0	7.5	6.0	4.3	5.0	3.3	3.8	2.3	3.0	2.5
Time OFF (s)	10.0	15.0	12.0	12.9	20.0	13.3	22.5	13.8	24.0	25.0
Polycrystalline silicon Flow rate (g/s)	**Calculated Feed Rate (kg/hr)**									
5	9.0	6.0	6.0	4.5	3.6	3.6	2.6	2.6	2.0	1.6
10	18.0	12.0	12.0	9.0	7.2	7.2	5.1	5.1	4.0	3.3
15	27.0	18.0	18.0	13.5	10.8	10.8	7.7	7.7	6.0	4.9
20	36.0	24.0	24.0	18.0	14.4	14.4	10.3	10.3	8.0	6.5
25	45.0	30.0	30.0	22.5	18.0	18.0	12.9	12.9	10.0	8.2
30	54.0	36.0	36.0	27.0	21.6	21.6	15.4	15.4	12.0	9.8
35	63.0	42.0	42.0	31.5	25.2	25.2	18.0	18.0	14.0	11.5

The feed rate is calculated according to the following expression:

$$FeedRate\left({}^{kg}\!/_{hr}\right) = \frac{3600\,({}^{s}\!/_{hr}) \times Time\,On\,(s) \times Polysilicon\,Flow\,Rate\,({}^{g}\!/_{s})}{[Time\,On\,(s) + Time\,Off\,(s)] \times 1000\,({}^{g}\!/_{kg})}$$

By way of example, the 3, 7 and 13 segment deposition patterns are depicted in FIGS. 9a, 9b and 9c , respectively.

Although the foregoing discussion is directed to the initial charging (loading and feeding of polycrystalline silicon) and meltdown of the polycrystalline silicon to form a silicon melt in a crucible, the present invention is also directed to the recharging of a crucible containing a depleted molten silicon charge. A depleted molten charge is typically formed by pulling a single crystal silicon ingot from a previously formed silicon melt; a portion of the silicon melt remains in the crucible after the ingot is separated from the silicon melt. Preferably, the ingot pulled from the previously formed silicon melt leaves a depleted molten silicon charge having a weight (*w*) that is about 15% to about 40% by weight of the silicon melt that is to be formed by the recharge. More preferably, weight of the depleted molten silicon charge (*w*) is about 20% to about 30% by weight of the silicon melt that is to be formed by the recharge. In accordance with the present invention, polycrystalline silicon is fed into the rotating crucible by delivering the polycrystalline silicon onto the depleted molten silicon charge to form a partial charge comprising molten silicon and unmelted polycrystalline silicon, the molten silicon comprising an upper surface, the unmelted polycrystalline silicon comprising an exposed portion that is above the surface of the molten silicon, the exposed unmelted polycrystalline silicon having a center and width, *d*, that corresponds to the longest distance between two points along the interface between the exposed unmelted polycrystalline silicon and upper surface of the molten silicon. The polycrystalline silicon fed into the crucible to form the partial charge may be fed by any appropriate method (e.g., by continuous feed and/or by intermittent delivery). Preferably, however, the partial charge is formed in accordance with the intermittent delivery described in detail herein. For example, to rapidly build up the exposed unmelted polycrystalline silicon it may be beneficial to frequently deposit polycrystalline silicon on particular portions of the depleted molten silicon and/or exposed unmelted polycrystalline silicon such as depicted in FIGS. 8b and 8c. The recharging process continues by feeding polycrystalline silicon into the

rotating crucible by intermittently delivering polycrystalline silicon onto the exposed unmelted polycrystalline silicon thereby maintaining the width of the exposed unmelted polycrystalline silicon (d) as described in detail herein. The unmelted polycrystalline silicon and the intermittently delivered polycrystalline silicon are melted to form the silicon melt.

Example 1

About 40 kg of chunk polycrystalline that was loaded into a 20 inch (51 cm) diameter crucible and heated to form molten silicon and unmelted polycrystalline silicon. A vertical-type feed tube positioned slightly off the centerline of the crucible (about 15 mm) and approximately 10 inches (25 cm) above the melt surface was used to feed about 40 kg of granular polycrystalline silicon into the crucible for a total charge of about 80 kg. The granular polycrystalline silicon flow rate (f) was approximately 17 grams/second from the hopper, through the injector tube and into the crucible.

The furnace side heater power was about 118 kW and the crucible rotation rate (r) was about 2 RPM. The chunk polycrystalline silicon was partially melted after about 3.5 hours (i.e., the diameter of the chunk polycrystalline island, centered in the crucible, was about 75% of the crucible diameter). Initially, the duration of the on-period (t_{on}) was set to about 5 seconds and the duration of the off-period (t_{off}) was set to about 20 seconds to yield a feed rate (F) of about 11.5 kg/hr. The initial on/off-period combination was chosen to provide a feed rate that, based upon experience with continuous feeding, would maintain the width (d) of the unmelted polycrystalline silicon (island) diameter of the island at about 75% of crucible diameter (D) (i.e., about 38 cm). The foregoing settings resulted in the 6 segment feed pattern depicted in FIG. 8a.

At the t_{on}/t_{off} settings of 5s/20s, the melting rate was much faster than expected and the exposed unmelted polycrystalline silicon (island) shrank in size to less than about 75% of the crucible diameter. After about 1 hour, the t_{off} was

decreased to about 15 seconds to yield a feed rate of about 14.5 kg/hr. With this t_{on}/t_{off} combination, the island grew quickly in size to about 75% of the crucible diameter. After about 2 hours at the 5s/15s setting (depicted in FIG. 8b), it was necessary to reduce the t_{off} to about ten seconds to maintain the diameter of the island at about 75% of the crucible diameter. The 5s/10s combination (depicted in FIG. 8c) resulted in a feed rate of about 19.2 kg/hr. The 40 kg granular polycrystalline silicon addition was completed in about 3 hours and 15 minutes and the island completed melting after another 30 minutes. The total melting time was about 7 hours and 15 minutes.

Compared to continuously feeding granular polycrystalline silicon onto a chunk polycrystalline silicon initial charge which can typically feed/melt granular polycrystalline at about 8-12 kg/hr while maintaining the width of the island at about 75% of the crucible diameter, the melting rate of the granular polycrystalline silicon fed at 5s/20s was surprisingly fast (i.e., the island was shrinking in size below about 75% of the crucible diameter). Surprisingly, the feeding/melting rates at 5s/15s and 5s/10s were surprisingly slow for a melt mass that had been increased to about 52 kg and 60 kg, respectively.

Example 2

Based on the test detailed in Example 1, it was determined that the intermittent feeding process can significantly increase the feed rate (F) at which an appropriate island width may be maintained thereby decreasing the feed time compared to a continuous feed process. Specifically, it was determined that maximizing the degree of rotation between subsequently deposited wedges and maximizing number of on-periods before redepositing feed material on a particular portion, or segment, of the polycrystalline island greatly increased the flow rate at which the 75% crucible diameter island size could be maintained.

In view of the foregoing principles, an optimum set of parameters were determined and tested in order to maximize the feeding/melting rate of granular

polycrystalline silicon into the loaded crucible. As in Example 1, the crucible was initially loaded with 40 kg of chunk polycrystalline silicon, the gravity feeder delivered granular polycrystalline silicon at a flow rate (*f*) of about 17 g/s and the side heater power was at about 118 kW. A deposition pattern depicted in FIG. 10 was selected along with an on/off-period combination of about 5s/12s. It was determined that crucible should be rotated at a rate (*r*) of about 2.1 rpm, based on the following expression :

RPM = 60s/(1 x number of seconds ON + 2 x number of seconds OFF).

In accordance with the foregoing parameters the granular polycrystalline was fed at a rate (*F*) of about 20 kg/hr onto the exposed unmelted polycrystalline (island) while maintaining a width of the island at about 75% of the crucible diameter. Thus, the intermittent feeding process reduced the feeding time to about 2 hours which is about half of the time required for a continuous feeding process.

In light of the detailed description of the invention and the examples presented above, it can be appreciated that the several objects of the invention are achieved.

The explanations and illustrations presented herein are intended to acquaint others skilled in the art with the invention, its principles, and its practical application. Those skilled in the art may adapt and apply the invention in its numerous forms, as may be best suited to the requirements of a particular use. Accordingly, the specific embodiments of the present invention as set forth are not intended as being exhaustive or limiting of the invention.

When introducing elements of the present invention or the preferred embodiment(s) thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.